

NO DRAWINGS

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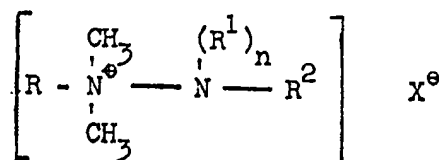
(54) SUBSTITUTED HYDRAZINE DERIVATIVES AND AGENTS
CONTAINING THEM FOR RETARDING THE GROWTH
OF PLANTS

(71) We, BADISCHE ANILIN- & SODA-FABRIK AKTIENGESELLSCHAFT, a German Joint Stock Company, of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

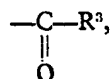
The present invention relates to new and valuable substituted hydrazine derivatives and to agents containing them for regulating the growth of plants. It relates in particular to agents which reduce the growth height of plants.

It is known to influence the plant habit, e.g. with N,N-dimethyl-(2-chloroethyl)-hydrazinium chloride; however, this compound is not always satisfactory in practice for various reasons.

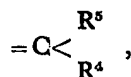
We have now found that hydrazine derivatives having the formula



where R denotes a lower aliphatic, linear or branched, saturated or unsaturated, substituted or unsubstituted radical having at most five carbon atoms which it attached by means of a carbon atom (e.g. β -halo-ethyl, methyl, ethyl, isopropyl, sec-butyl, allyl, 2-chloroallyl, 2-methallyl, butyn-(1)-yl-(3), cyclopropylmethyl radical), R¹ denotes a hydrogen atom, R² denotes a substituted or unsubstituted alkenyl radical of 2 to 4 carbon atoms or a substituted or unsubstituted benzyl radical or the radical

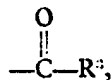


R³ denoting hydrogen or an aliphatic (e.g. methyl, ethyl, propyl, chloromethyl, cyanomethyl, δ -chlorobutyl, ϵ -chlorocapryl, methoxymethyl, ethoxymethyl, 1,1-dimethylacetoxymethyl, 1,1-dimethylethyl, isobutyl, vinyl, or α -propenyl, or a carbocyclic radical) e.g. a cycloaliphatic (e.g. cyclohexyl radical) or carbocyclic aromatic radical (e.g. phenyl, 4-chlorophenyl, 2,4-dichlorophenyl, 2-tolyl, 4-tolyl, 4-methoxyphenyl radical) or the pyridyl radical, or R¹ and R² together denote the radical



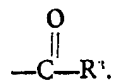
R⁵ denoting hydrogen or the same radicals as R⁴, R⁵ and R⁴ being identical or different, and R⁴ denoting an aliphatic cycloaliphatic or monocyclic aryl radical X[⊖] denotes a

non-phytotoxic anion, e.g. bromide, chloride or methosulfate, and n denotes one, or in the case where R² denotes the radical



n may be zero and X⁻ denote a unit negative charge on the nitrogen atom to which R² is attached.

5 Preferably the radicals denoted by R, R², R³, R⁴ and R⁵ are free from unspecified substituents other than chlorine atoms or hydrocarbon or chlorohydrocarbon radicals. Advantageously the substituted hydrazine contains from 4 to 21 carbon atoms and R and R³ are free from substituents other than chlorine atoms or cyano, alkoxy, aryloxy, alkanoyloxy hydrocarbon or chlorohydrocarbon radicals and R² denotes the radical

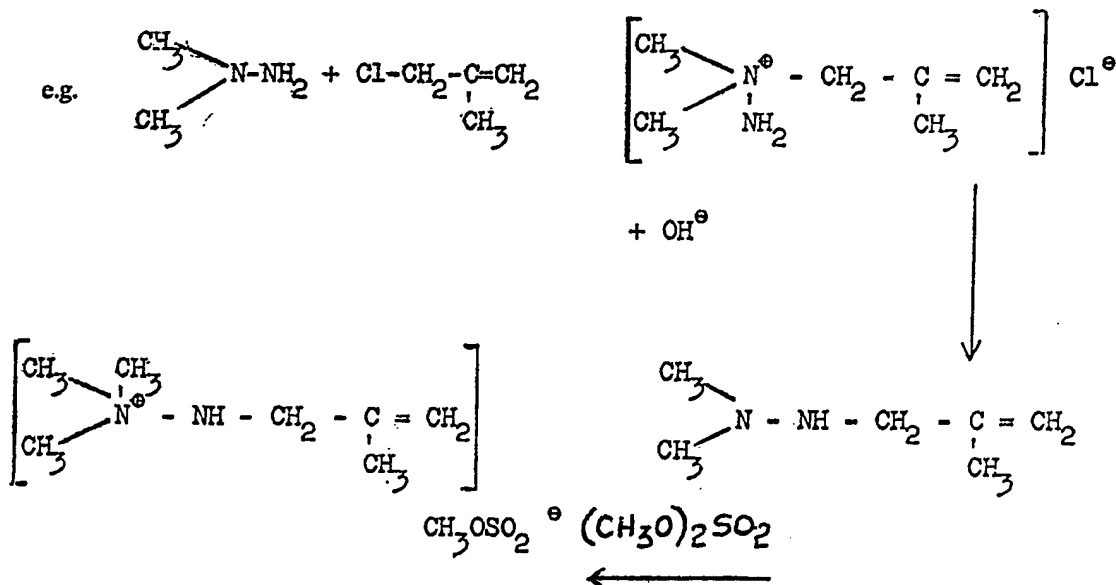


Alternatively R² may advantageously be a 2- alkenyl radical of from 3 to 6 carbon atoms optionally substituted by from 1 to 3 chlorine atoms.

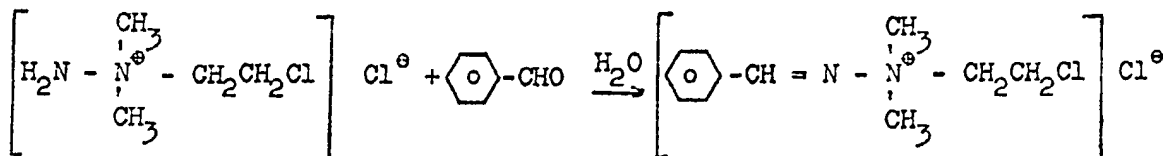
15 A useful subclass of active compounds according to the invention is one in which the radicals R, R² and R³ are as specified in one of the above advantageous subclasses except that one of the said radicals although still attached by means of a carbon atom contains an ether link but not a heterocyclic ether link.

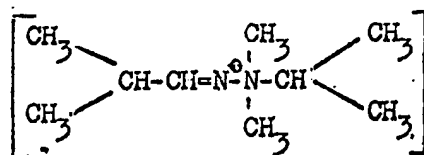
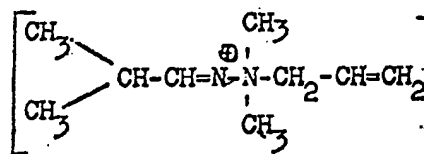
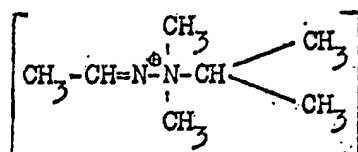
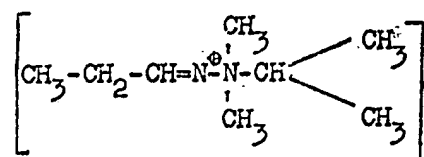
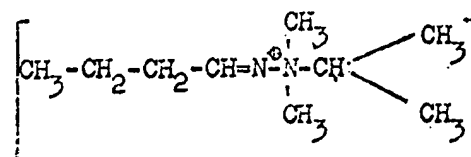
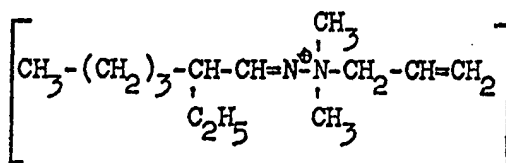
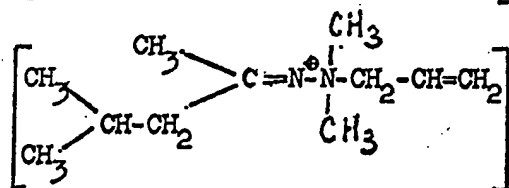
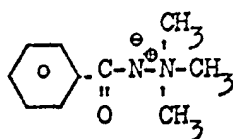
The products according to the invention may be produced by various processes, some of which are briefly described in the following:

20 1) By alkylating an asymmetric hydrazine and subsequent alkaline treatment, a tri-substituted hydrazine is obtained which is converted into a N,N,N'-tetrasubstituted hydrazinium salt by repeated alkylation:

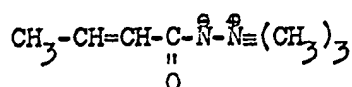


25 2) Reaction of N,N,N-trisubstituted hydrazinium salts with aldehydes or ketones:

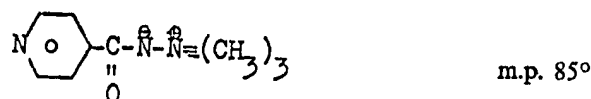


Br[⊖] m.p. 146° to 148°CBr[⊖] m.p. 64° to 65°CBr[⊖] m.p. 116° to 117°CBr[⊖] m.p. 118° to 120°CBr[⊖] m.p. 106° to 108°CBr[⊖] m.p. 40°CBr[⊖] m.p. 88° to 89°C

m.p. 162° to 163°C

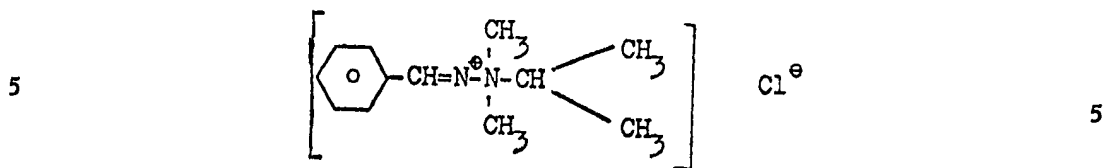


m.p. 157° to 158°C



EXAMPLE 3

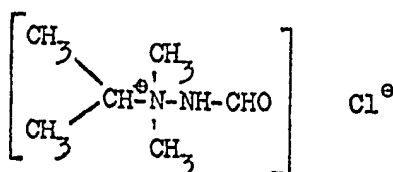
Adopting the procedure described in Example 2,



having a melting point of 158° to 159°C is obtained from benzaldehyde and N,N-dimethyl-N-isopropylhydrazinium chloride.

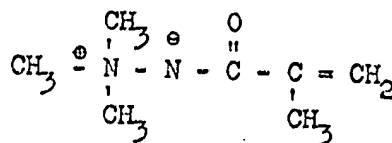
EXAMPLE 4

126 parts by weight of N,N-dimethyl-N-isopropylhydrazinium chloride is dissolved in acetonitrile, 54 parts by weight of methyl formate is added, and, at 40° to 50°C , 162 parts by weight of 30% methanolic sodium methylate solution is dripped in. The whole is stirred for three hours at 60°C and suction filtered. The filtrate is acidified with 34 parts by weight of concentrated hydrochloric acid and concentrated. After recrystallization from acetone/alcohol, the compound has a melting point of 142° to 143°C .

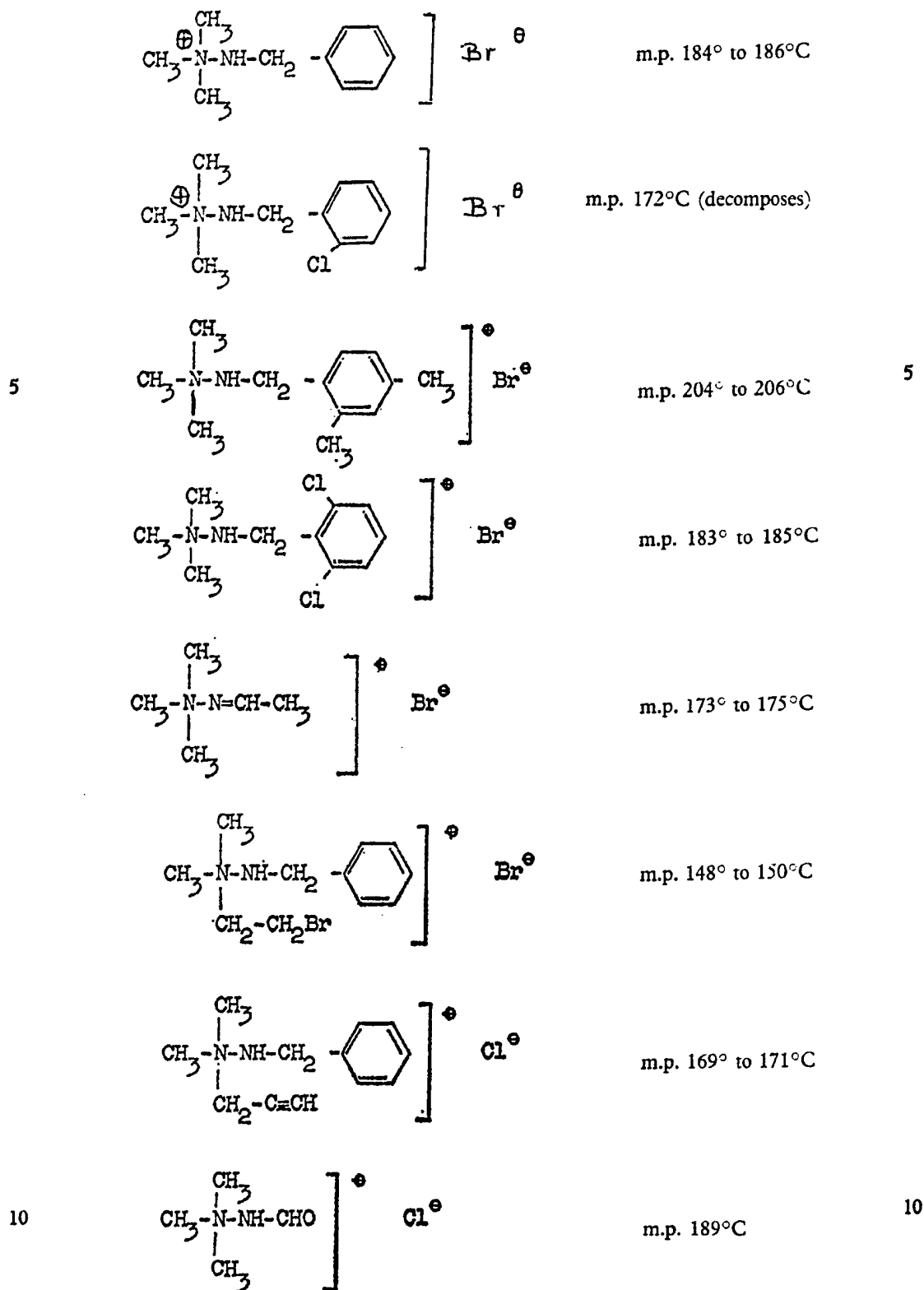


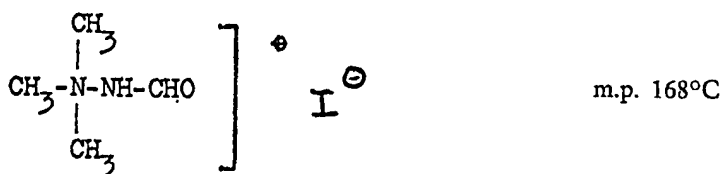
EXAMPLE 5

47 parts by weight of N,N,N-trimethylhydrazinium bromide is dissolved in 225 parts by weight of tert-butanol; 30 parts by weight of methyl methacrylate and 16 parts by weight of sodium methylate are dripped in. After heating for six hours at 50°C , the reaction product is suction filtered, concentrated and recrystallized from benzene. The end product has a melting point of 149° to 150°C and the following formula:



The following compounds are further examples of the active ingredients according to the invention:





The products according to the invention reduce the growth height of plants and may act either through the soil or through the foliage of the plants. They may also be applied to the seeds before planting.

The agents for regulating plant growth according to this invention may be used as solutions, emulsions, suspensions or dusts. The form of application depends entirely on the purpose for which the agents are being used; in any case it should ensure a fine distribution of the active ingredient.

For the preparation of solutions to be sprayed direct, the solution in water is suitable. However, hydrocarbons such as tetrahydronaphthalene and alkylated naphthalenes may also be used as spray liquids. Liquid hydrocarbons or hydrocarbon fractions having a boiling point above 150°C are preferred.

Aqueous formulations may be prepared from emulsion concentrates, pastes or wettable powders by adding water. To prepare emulsions, the ingredients as such or dissolved in a solvent may be homogenized in water or organic solvents by means of wetting or dispersing agents. Concentrates which are suitable for dilution with water may be prepared from active ingredient, emulsifying or dispersing agent and possibly solvent.

Dusts may be prepared by mixing or grinding the active ingredients with a solid carrier. The active ingredients may be mixed with plant nutrients or with oils of vegetable or animal origin.

The following comparative experiments, from which the mode of treatment and its results are apparent, demonstrate the superiority of the compositions according to this invention over known active ingredients.

EXAMPLE 6

100 grains of the wheat type "Opal" were sown in a loamy sandy soil in Neubauer dishes; the dishes were treated immediately after sowing with three of the active ingredients according to the invention in aqueous solution together with a wetting agent (polyalkylene oxide adduct) at application rates corresponding to 3 to 12 kg of active ingredient per hectare. The prior art growth retardant N-dimethyl-N-(β -chloroethyl)-hydrazinium chloride (CMH) was used for comparison purposes in addition to untreated control dishes.

A few days after emergence of the plants a marked reduction in growth height compared with the control was observed which was much more pronounced in the case of the active ingredients according to the invention than in that of the standard substance CMH. The differences in growth height were determined after three weeks and are given in the following table.

	Active ingredient application rate kg/ha	growth height of the wheat	
		in cm	relative
control (untreated)	—	27.3	100
N-dimethyl-N-(β -chloroethyl)- hydrazinium chloride (CMH)	3	24.0	88
N-dimethyl-N-(β -chloroethyl)- hydrazinium chloride (CMH)	12	22.0	81
N-trimethyl-N'-allylhydrazinium bromide	3	23.5	86
N-trimethyl-N'-allylhydrazinium bromide	12	20.5	75
N-trimethyl-N'- α -chloroallylhydra- zinium chloride	3	21.5	79
N-trimethyl-N'- α -chloroallylhydra- zinium chloride	12	19.0	70
N-trimethyl-N'- α -methylallylhydra- zinium bromide	3	20.5	75
N-trimethyl-N'- α -methylallylhydra- zinium bromide	12	19.0	70

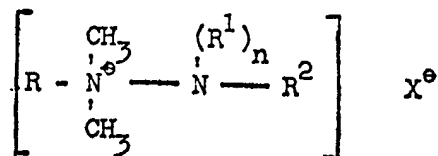
EXAMPLE 7

In the same way as in Example 6, grains of the rye type "Petkuser" were sown. In this case, treatment was carried out with the same active ingredients in admixture with a nutrient (urca) but at a height of the plants of 8 to 9 cm. The effect on rye was not as marked as that on wheat. Compared with the prior art active ingredient CMH, the active ingredients according to this invention had a stronger action, as may be seen from the following table.

	Active ingredient application rate kg/ha	growth height of the rye	
		in cm	relative
control (untreated)	—	31.3	100
N-dimethyl-N-(β-chloroethyl)-hydrazinium chloride (CMH)	3	30.5	97
N-dimethyl-N-(β-chloroethyl)-hydrazinium chloride (CMH)	12	30.0	96
N-trimethyl-N'-allylhydrazinium bromide	3	30.0	96
N-trimethyl-N'-allylhydrazinium bromide	12	29.5	94
N-trimethyl-N'-α-chloroallylhydrazinium chloride	3	29.0	93
N-trimethyl-N'-α-chloroallylhydrazinium chloride	12	29.5	94
N-trimethyl-N'-α-methylallylhydrazinium bromide	3	29.5	94
N-trimethyl-N'-α-methylallylhydrazinium bromide	12	29.0	93

WHAT WE CLAIM IS:—

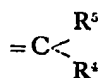
1. A substituted hydrazine derivative having the formula



where R denotes an aliphatic radical of 1 to 5 carbon atoms which is attached by means of a carbon atom, R¹ denotes a hydrogen atom, R² denotes a substituted or unsubstituted alkenyl radical of 2 to 4 carbon atoms, or a substituted or unsubstituted benzyl radical, or the radical



where R³ denotes hydrogen, or a pyridyl or a carbocyclic radical or a saturated or olefinically unsaturated aliphatic hydrocarbon radical which is substituted by a cyano, chloro, methoxy, ethoxy or acetoxy group, or R¹ and R² together denote the radical



where R^4 denotes an aliphatic or cycloaliphatic radical or a monocyclic aryl radical, and R^1 denotes hydrogen or may independently denote any of the radicals denoted by R^4 , and $n=1$ and X^\ominus denotes an anion; or, in the case where R^2 denotes the radical $C-R^3$, n may be zero and X^\ominus then denotes a unit negative charge on the nitrogen

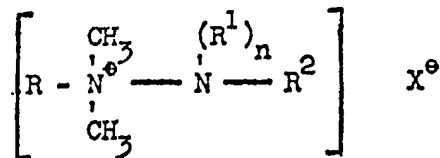
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atom to which R^2 is attached.

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2. A substituted hydrazine derivative having the formula



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where R denotes a lower aliphatic, linear or branched, saturated or unsaturated substituted or unsubstituted radical having at most five carbon atoms, R^1 denotes a hydrogen atom, R^2 denotes a substituted or unsubstituted lower alkenyl radical having 2 to 4 carbon atoms, or a substituted or unsubstituted benzyl radical or the radical $C-R^3$, R^3 denoting hydrogen or an alkyl radical of 1 to 4 carbon or a cycloaliphatic

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or aromatic radical or the pyridyl radical; or R^1 and R^2 together denote the radical

$=C<\overset{R^5}{\underset{R^4}{}}$, R^4 denoting an aliphatic or cycloaliphatic radical, or a monocyclic aryl

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radical, R^5 denoting hydrogen or the same radicals as R^4 , and R^3 and R^4 being identical or different, X denotes a non-phytotoxic anion and n denotes one of the integers 0 and 1.

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3. A substituted hydrazine derivative as claimed in claim 1 or 2 in which R^4 , if present, denotes an aliphatic or cycloaliphatic radical.

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4. A substituted hydrazine derivative as claimed in any preceding claim in which the radicals denoted by R , R^2 , R^3 , R^4 and R^5 are free from unspecified substituents other than chlorine atoms or hydrocarbon or chlorohydrocarbon radicals.

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5. A substituted hydrazine derivative as claimed in claim 1, 2 or 3 which contains from 5 to 21 carbon atoms and in which R and R^3 are free from substituents other than chlorine atoms or cyano, alkoxy, aryloxy, alkanoyloxy, hydrocarbon or

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chlorohydrocarbon radicals and R^2 denotes the radical $C-R^3$.

6. A substituted hydrazine derivative as claimed in claim 4 in which R^2 is a 2-alkenyl radical of from 3 to 6 carbon atoms optionally substituted by from 1 to 3 chlorine atoms.

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7. A substituted hydrazine derivative as claimed in claim 1 or 2, in which the radicals R , R^2 and R^3 are as specified in claim 5 or 6 except that one of the said radicals although still attached by means of a carbon atom contains an ether link but not a heterocyclic ether link.

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8. A substituted hydrazine as claimed in claim 1 or 2 in which R^1 and R^2

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together denote $=C<\overset{R^5}{\underset{R^4}{}}$, and R denotes a secondary alkyl radical.

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9. A substituted hydrazine derivative as claimed in claim 1 or 2 and listed herein.

10. N,N,N -trimethyl- N' -allylhydrazinium bromide.

11. N,N,N -trimethyl- N' -(α -methallyl)-hydrazinium bromide.

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12. N,N,N -trimethyl- N' -(α -chloroallyl)-hydrazinium bromide.

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13. A process for the preparation of a substituted hydrazine derivative as specified in claim 1 or 2 by alkylating an N,N,N' -trisubstituted hydrazine derivative, by reaction of an N,N,N -trisubstituted hydrazinium salt with an aldehyde, ketone, or an ester or other amide-forming acid derivative or by quaternisation of a hydrazone or by inter-conversion of an inner nitrogen ylide and the corresponding hydrazinium amide salt.

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14. A process for the preparation of a substituted hydrazine derivative as claimed in claim 1 or 2 substantially as described herein.

15. A plant growth regulating composition comprising a solid or liquid carrier and a substituted hydrazine derivative as claimed in any of claims 1 to 12.
- 5 16. A plant growth regulating composition as claimed in claim 15 in which the carrier is an inert solid or a liquid hydrocarbon or hydrocarbon fraction having a boiling point above 150°C. 5
17. A plant growth regulating composition as claimed in claim 15 in which the carrier comprises an oil of vegetable or animal origin.
18. A plant growth regulating composition containing a substituted hydrazine derivative as claimed in claim 1 or 2 and a plant nutrient.
- 10 19. A plant growth regulating composition containing a substituted hydrazine derivative as claimed in claim 1 or 2 and a wetting agent. 10
20. A process for preparing a plant growth regulating composition as claimed in any of claims 15 to 19 which comprises mixing the active compound with a solid or liquid carrier.
- 15 21. A process for regulating the growth of crop plants wherein the plants or the seeds or the soil in which the plants are growing or are to grow are treated with a hydrazine derivative as claimed in claim 1 or 2. 15
22. A process as claimed in claim 21 in which the plants or seeds are cereals.
- 20 23. A process for regulating the growth of crop plants substantially as described herein. 20

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